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Application of Central Composite Design approach for dairy wastewater treatment by electrocoagulation using iron and aluminum electrodes: modeling and optimization

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ABSTRACT

In this study, response surface methodology approach using Central Composite Design was applied to develop a mathematical model and to optimize process parameters for the COD, color, orthophosphate, TSS, and turbidity removal from dairy wastewater by electrocoagulation process using iron and aluminum electrodes. The second-order regression model was developed to predict the removal efficiencies using Statgraphics Centurion XVI.I software program. The optimum conditions for the COD removal were found to be 5.06 min for reaction time, 5.0 for pH, and 50.5 A/m^2 for current density with Al electrodes, whereas 5.21 min for reaction time, 5 for pH, and 65 A/m^2 for current density with Fe electrodes. High removal efficiencies (98.91% COD and 99.78% orthophosphate removal with Al electrodes, and 98.84% COD and 98.24% orthophosphate removal with Fe electrodes) were achieved under optimum conditions. The operating costs for the COD removal from dairy wastewater by electrocoagulation process using Fe and Al electrodes at optimized conditions were calculated to be 0.54 and 0.42 €/m^3, respectively. The sludge formed under optimized conditions in EC process was characterized by Fourier Transform Infrared Spectroscopy (FT-IR) analysis. The FT-IR results showed that pollutants in dairy wastewater were linked with aluminum hydroxide and iron hydroxide complexes, precipitated at the bottom of the reactor containing milk components.

Keywords: Dairy wastewater; Electrocoagulation; RSM; Cost analysis; Sludge characterization

1. Introduction

The dairy industry is one of the most polluting industries in food processing in terms of the volume of effluent generated and its characteristics, because milk processing results in high organic matter content [1,2]. Dairy wastewater is distinguished by high levels of dissolved and suspended solids including fats, oils and grease, and nutrients, such as ammonia and phosphates, and high BOD and COD contents [3]. One of the main components of the dairy wastewater is milk, consisting of three parts: (i) an oil-in-water emulsion in which the fat droplets are dispersed in the serum, (ii) a colloidal suspension of casein micelles, protein, and lipoprotein particulates and the (iii) aqueous phase containing soluble proteins, mineral salts, and vitamins [4]. A huge amount of wastewater, approximately 0.2 to 10 L of wastewater per liter of

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processed milk is generated [5,6] and generally process effluents are discarded into rivers without any treatment causing eutrophication due to phosphorus and nitrogen compounds [6,7]. Phosphorus and nitrogen compounds discharge is responsible for the dramatic growth of algae in internal and coastal waters [7]. This affects water quality through the consumption of dissolved oxygen, destroying aquatic life [8,9]. Discharge of high organic matter into water media results in excess consumption of oxygen by bacteria. Oxidation of effluent by bacteria results in depletion of oxygen in water, faster than oxygen gain from air. This problem leads to inadequate maintenance of higher life forms [10]. Additionally, wastewater consisting excessive amount of fats and oils can cause the formation of surface films and shoreline deposits and can lead to environmental degradation when discharged to water media [11]. Treating dairy effluents is, thus, of crucial importance for the environment and for the purpose of recycling water in industrial processes [6,12].

Many physicochemical and biological methods are used to treat dairy effluents. However, aerobic biological processes are high energy-intensive processes, whereas anaerobic biological process effluents need additional treatment before final discharge [1]. All compounds of dairy wastewater are biodegradable, except protein and fats, which are not easily degraded by biological treatment, especially using anaerobic treatment [13,14]. The presence of fats shows inhibitory action during anaerobic treatment of dairy wastewaters [15]. Anaerobic processes are also prone to shock loading. In aerobic biological processes, large amounts of biomass are produced, besides high energy requirement [16]. On the other hand, physical/chemical methods have the disadvantage of high reagent costs and low COD removal [6,17]. Moreover, chemical treatment could induce a secondary pollution due to the chemical additives. The wastewater generated in food industries can be treated using different techniques which should allow either its reuse or its direct disposal into the sewer system [3,18–20]. In recent years, among different techniques used for industrial wastewater treatment, the electrochemical methods have been applied widely [11,21,22]. Rajeshwar et al. [23] listed the benefits of electrochemical techniques as environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost-effectiveness. Additionally, electrochemical techniques offer easy applicability and require minimum amount and number of chemicals [24]. Electrochemical-based systems allow controlled and rapid reactions and the systems employ only electrons to facilitate wastewater treatment instead of using chemicals and micro-organisms [24]. The sludge generated by electrochemical processes is relatively low and tends to be readily settleable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Kobya et al. [25] concluded that sludge, produced in electrocoagulation process of textile wastewater, varied between 0.65 and 1.00 kg/m^3 for iron and 0.90–1.30 kg/m^3 for aluminum electrodes, respectively. Arslan-Alaton et al. [26] concluded that sludge production rate was lower with stainless steel (700 g/m^3) as compared with aluminum (8.200 g/m^3) electrodes in electrocoagulation of simulated acid dyebath effluent. Sivakumar et al. [27] investigated the comparison of sludge volume generated by the electrocoagulation and chemical coagulation processes and concluded that sludge volumes were 2.6 mL/L in electrocoagulation process and 10.6 mL/L in the chemical coagulation process, respectively. Among the electrochemical techniques, there is much interest in using electrocoagulation for industrial wastewater treatment.

Electrocoagulation (EC) is an electrochemical technique closely related to chemical coagulation, which involves the supply of coagulant ions (Al^{3+}, Fe^{3+}) by the application of an electric current to a sacrificial anode placed in a process reactor [21].

EC process involves three successive stages [24,28]:

(i) Formation of coagulants by electrolytic oxidation of the electrode.

The main reaction occurring at the metal anode is dissolution:

$$M(s) \rightarrow M(aq)^{n+} + ne^- \quad (1)$$

Additionally, water electrolysis occurs at the cathode and anode as shown in Eqs. (2) and (3):

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(\text{cathodic reaction}) \quad (2)$$

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-(\text{anodic reaction}) \quad (3)$$

(ii) Destabilization of the contaminants, particulate suspension, and breaking of emulsions. A direct electrochemical reduction of metal cations (M^{n+}) may occur at the cathode surface:

$$M^{n+} + ne^- \rightarrow nM^0 \quad (4)$$

Furthermore, the hydroxide ions formed at the cathode increase the pH of the wastewater, thereby inducing the precipitation of metal ions as corresponding hydroxides and co-precipitation with hydroxides:

$$M^{n+} + nOH^- \rightarrow M(OH)_n(s) \quad (5)$$

(iii) Aggregation of the destabilized phases to form flocs.

Optimizing the electrocoagulation process implies the determination of the experimental conditions in wastewater treatment. In conventional multifactor experiments, optimization is usually carried out by varying one factor while all other factors are kept fixed at a specific set of conditions. Since the classical optimization technique does not represent the effect of interactions between different factors, it is incapable of reaching the true optimum. Recently, statistical design of experiments is used to consider interactions among the variables to optimize the operating parameters in multivariable systems and to obtain statistically significant models by performing minimum number of experiments [29]. Response surface methodology (RSM) is a useful statistical technique for modeling and analysing the problems in which a response of interest is influenced by several variables, with the objective of optimizing this response [29,30]. Central Composite Design (CCD), the most commonly used design under RSM, is an efficient and flexible method in providing sufficient data on the effects of variables and overall experiment error with minimum number of experiments [29].

Few studies have been carried out by studying the application of electrocoagulation in wastewater treatment produced by food industries. In the present work, electrocoagulation process using aluminum and iron electrodes were used for dairy wastewater treatment. RSM was employed to determine the optimal conditions (pH, current density, and reaction time) for the COD, color, orthophosphate, TSS, and turbidity removal. The experimental runs were designed in accordance with CCD. Overall operational cost analyses were also determined.

2. Materials and methods

2.1. Wastewater characterization

Real wastewater from milk-processing factory was used in this study. The characterization of dairy wastewater is given in Table 1. The contaminant concentrations of the dairy wastewater given in Table 1 are determined to be consistent with the results of the studies in literature [13,31]. Before the EC treatment, the dairy effluents were preserved and analyzed according to the Standard Methods recommended by the American Public Health Association [32]. The effluent characterization of dairy wastewater, treated by electrocoagulation process under optimum conditions, is also shown in Table 1.

2.2. Experimental setup and procedure

A laboratory-scale plexiglass EC reactor with 9 cm diameter and 13 cm height was constructed. Electrode sets (two anode and two cathode electrodes) comprised of four monopolar (MP) parallel aluminum plates (6 cm width × 11.5 cm height and 0.1 cm thickness), each having an effective area of 46.2 cm^2. The electrodes were placed 1.5 cm apart from each other. A valve was installed at the bottom of the reactor to withdraw the precipitated material through a sludge chamber. For each test, 600 mL wastewater sample was used. Electrolyte solution was not used, since salinity of the wastewater samples was found to be sufficient. Before each run, electrodes were washed with acetone and the impurities on the aluminum electrode surfaces were removed by dipping in a solution freshly prepared by mixing 100 cm^3 of HCl solution (35%) and 200 cm^3 of hexamethylenetetramine aqueous solution (2.80%) for 5 min [33].

All the chemicals used were of analytical-reagent grade. The electrocoagulation experiments were initiated by supplying a current density of 25–65 A/m^2 to the effluent for 45 min by means of a DC power supply. At the end of each run, the floated and precipitated materials were withdrawn and the clarified effluent sample was pipetted out from the reactor and then allowed to settle for a few hours in a polyethylene flask. Finally, the clarified supernatant liquid was collected and preserved according to the Standard Methods [32] and stored for characterization.

The sludge formed during EC process was characterized by the Fourier Transform Infrared Spectroscopy (FT-IR, Schimadzu 8900). An amount of the sample was dispersed in spectroscopic grade KBr to record the spectra. IR spectra were recorded in the range of 4,000–650 cm^{-1}.

2.3. Experimental design and model development

Three analytical steps; adequacy of various model tests (sequential model sum of squares and model summary statistics), analysis of variance (ANOVA), and the response surface plotting were performed to establish an optimum condition for the COD and TSS removal from the dairy wastewater. For the statistical design of experiments and data analysis, the Statgraphics Centurion XVI.I software programme was used. The full-factorial CCD based on RSM was used

Table 1
Characterization of dairy wastewater

	Dairy influent		Dairy effluent*	
Parameters	Range	Mean value ± SD	Range	Mean value ± SD
Number of samples	7	7	7	7
pH	6.78–7.07	6.9 ± 0.093	7.21–7.26	7.23 ± 0.017
COD (mg/L)	783–792	788 ± 3.656	8.55–8.69	8.61 ± 0.046
TSS (mg/L)	91–98	94 ± 2.422	6.8–7.5	7.2 ± 0.238
Turbidity (NTU)	465–481	473 ± 5.879	5.95–6.4	6.2 ± 0.166
Chloride (mg/L)	76–81	79 ± 1.635	87.9–89	88.7 ± 1.122
Orthophosphate (mg/L)	6.87–7.01	6.91 ± 0.0512	0.021–0.026	0.024 ± 0.0016
Color (Pt/Co)	429–441	436 ± 4.718	7.2–7.8	7.5 ± 0.211
Conductivity (mS/cm)	2.11–2.15	2.12 ± 0.015	2.25–2.28	2.27 ± 0.0125

*The effluent characterization in the best operating conditions.

in this study and a total of 20 experiments were conducted. Three operational parameters; J: 25–65 A/m^2, t_{EC}: 5–45 min, and pH: 5–9 were taken as input parameters whereas, COD, color, orthophosphate, TSS, and turbidity removal ratios were taken as responses of the system (Y). Table 2 represents the variables and their levels, whereas the actual experimental design matrix is given in Table 3. The ranges and levels of the independent variables were determined from the preliminary experiments. CCD, an experimental design used by RSM to fit a model by least squares technique, was used for improving and optimizing the process using iron and aluminum electrodes. For statistical calculations, the levels for the three parameters (X_1 (pH), X_2 (J), and X_3 (t_{EC})) were coded as X_i according to the following relationship:

$$y = f(x_1, x_2, x_3, \ldots, x_n) \pm \varepsilon \quad (6)$$

where y is the response (yield), f is the response function, ε is the experimental error, and x_1, x_2, x_3, …, x_n are the independent variables.

RSM-based CCD works with the coded value for process variables. The relation between the coded form and the actual value can be written as follows:

$$\text{Coded value} = X_i = \frac{X_i - X_{\text{avg}}}{\Delta X} \quad (7)$$

where X_i is actual value of the ith factor in the actual units, X_{avg} is the average of the low and high values for the ith factor, and ΔX represents the step change. To get true functional relationship between independent variables and the response, a second-order polynomial was used to describe the effect of variables in terms of linear, quadratic, and cross product which can be written as:

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i<j}^{n} \sum_{j}^{n} b_{ij} X_i X_j + \beta \quad (8)$$

where i and j represent the linear and quadratic coefficients; b_0 is the coefficient constant, b_i is the linear coefficient, b_{ii} is the interactive coefficient, and b_{ij} is the quadratic coefficient. Each variable is investigated for individual and interactive effect on removal process. If Eq. (8) is written for three independent variables with Y as ultimate response in their coded values, the following equation can be obtained:

Table 2
The coded and actual values of variables of the experimental design matrix for electrocoagulation

		Coded factor				
Factor	Original factor (X)	−2	−1	0	+1	+2
pH	X_1	5	6	6.9	8	9
Current density (A/m^2)	X_2	25	35	45	55	65
Electrolysis time (min)	X_3	5	15	25	35	45

Table 3
The full-factorial design used for the electrocoagulation of dairy wastewater by Fe and Al electrodes

Run	Initial pH (X_1)	Current density (X_2)	Electrolysis time (X_3)	Initial pH (X_1)	Current density (X_2)	Electrolysis time (X_3)	Sludge volume mL/ 0.6 m^3 of wastewater		Final pH	
							Fe electrodes	Al electrodes	Fe electrodes	Al electrodes
1	−1	−1	−1	6	35	15	23	130	9.57	7.22
2	1	−1	−1	8	35	15	10	38	11.2	9.08
3	−1	1	−1	6	55	15	86	195	9.58	7.75
4	1	1	−1	8	55	15	4.5	32	10.24	9.2
5	−1	−1	1	6	35	35	67	390	10.09	8.41
6	1	−1	1	8	35	35	10	150	11.79	9.5
7	−1	1	1	6	55	35	82	177	10.38	7.42
8	1	1	1	8	55	35	15	64	11.24	9.83
9	−2	0	0	5	45	25	115	320	8.99	7.72
10	2	0	0	9	45	25	12	56	11.53	9.87
11	0	−2	0	6.9	25	25	50	100	10.94	8.95
12	0	2	0	6.9	65	25	16	80	10.95	9.72
13	0	0	−2	6.9	45	5	13	36	9.62	7.38
14	0	0	2	6.9	45	45	38	120	10.77	9.24
15	0	0	0	6.9	45	25	23	82	10.71	9.52
16	0	0	0	6.9	45	25	17	265	10.62	9.2
17	0	0	0	6.9	45	25	12.5	190	10.44	9
18	0	0	0	6.9	45	25	12.5	191	10.44	8.9
19	0	0	0	6.9	45	25	12.5	192	10.44	9.1
20	0	0	0	6.9	45	25	12.5	190	10.44	9

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} {X_1}^2 + \beta_{22} {X_2}^2 + \beta_{33} {X_3}^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (9)$$

The predicted response (Y) (Eq. (8)) is correlated to the set of regression coefficients; (β): the intercept (β_0), the linear (β_1, β_2, β_3), the interactive (β_{12}, β_{13}, β_{23}), and the quadratic coefficients (β_{11}, β_{22}, β_{33}). The adequacy of the developed model was checked by the ANOVA technique. The quality of the fit of the polynomial model was expressed by R^2 and its statistical significance was checked by the Fisher F-test. The model terms were evaluated by p-value and F-value.

3. Results and discussion

3.1. Statistical analysis and optimization of operating parameters

3.1.1. Electrocoagulation using Fe electrodes

The second-order (quadratic) polynomial response surface model was applied to fit the experimental results obtained by CCD. Based on the experimental design results, the regression equations with the coded variables obtained for describing the COD, color, orthophosphate, TSS, and turbidity removal from dairy wastewater by electrocoagulation using Fe electrodes are presented as follows:

$$\text{COD removal}(\%) = 129.24 - 12.536 * X_1 + 0.5577 * X_2 - 0.8190 * X_3 + 1.7419 * {X_1}^2 - 0.3127 * X_1 X_2 - 0.0272 * X_1 X_3 + 0.0153 * {X_2}^2 + 0.0006 * X_2 X_3 + 0.0123 * {X_3}^2 \quad (10)$$

$$\text{Color removal}(\%) = -114.91 + 59.866 * X_1 + 0.2259 * X_2 - 0.3015 * X_3 - 3.8644 * {X_1}^2 - 0.0799 * X_1 X_2 - 0.0105 * X_1 X_3 - 0.0043 * {X_2}^2 + 0.0233 * X_2 X_3 - 0.0137 * {X_3}^2 \quad (11)$$

$$\text{Orthophosphate removal}(\%) = 96.570 + 0.6791 * X_1 + 0.0359 * X_2 + 0.0183 * X_3 - 0.1099 * {X_1}^2 + 0.0098 * X_1 X_2 + 0.0123 * X_1 X_3 - 0.0007 * {X_2}^2 - 0.0018 * X_2 X_3 - 0.0005 * {X_3}^2 \quad (12)$$

$$\text{TSS removal}(\%) = -87.165 + 35.346 * X_1 + 2.6705 * X_2 - 1.4273 * X_3 - 1.4515 * {X_1}^2 - 0.4132 * X_1X_2 + 0.1808 * X_1X_3 + 0.0034 * {X_2}^2 + 0.0053 * X_2X_3 + 0.0029 * {X_3}^2 \quad (13)$$

$$\text{Turbidity removal}(\%) = 94.742 + 2.8584 * X_1 - 0.1153 * X_2 - 0.2485 * X_3 - 0.4236 * {X_1}^2 + 0.0433 * X_1X_2 + 0.0519 * X_1X_3 - 0.0018 * {X_2}^2 - 0.0016 * X_2X_3 - 0.0007 * {X_3}^2 \quad (14)$$

The positive sign of the coefficients in Eqs. ((10)–(14)) indicates the synergistic effect, whereas the negative sign suggests antagonistic effect [34]. As can be seen from Eqs. ((10)–(14)), the individual operating variables, such as the initial pH of the solution and the electrolysis time have net negative effect on COD removal, whereas the current density has a net positive effect. The initial pH of the solution and the current density have net positive effects on color and TSS removal, whereas the electrolysis time has a net negative effect. The initial pH of the solution has net positive effect on turbidity removal, whereas the current density and the electrolysis time have net negative effects. All individual operating variables have positive effect on orthophosphate removal. It can be noted that the COD, color, orthophosphate, TSS, and turbidity removal efficiencies increases with the increase in the value of individual operating parameters that have positive sign of the coefficients and decreases with the decrease in the value of individual operating parameters that have negative sign of the coefficients. The removal efficiencies using Fe electrodes were predicted by Eqs. ((10)–(14)) and presented in Table 4. A considerable effect of the interaction among the variables was also observed.

Statistical testing of the model was evaluated by the ANOVA. The ANOVA of regression parameters of the predicted response surface quadratic model for the COD, color, orthophosphate, TSS, and turbidity removal by electrocoagulation process with Fe electrodes using the results of all experiments performed is given in Table 5. It can be noted that larger *F*-values indicated higher significance with the corresponding term. Furthermore, the *p*-value ("Prob > *F*") related to the *F*-value could be used to show whether the *F*-value is large enough or not. The *p*-values lower than 0.05 (at the significance level of 95%) confirm that the regression model is statistically significant [35,36]. Additionally, the sum of squares (SS) should also be checked while considering the significance of a particular variable. The significance of the variable increases with the increase in the SS value [34,37,38]. The "Prob > *F*" value lower than 0.0001 for the second-order polynomial fitting indicates that the model is statistically highly significant and that the model terms are significant with 95% probability level.

The model F value was found to be 9.28 with corresponding *p*-value of 0.00086 and high SS value, implying that the model is significant and can appropriately explain the relationship between the response and the independent variables for COD removal (Table 5). It can be concluded that the linear coefficients were found to be more significant than the quadratic and the interacting coefficients. The ANOVA study suggested that the electrolysis time has the most significant effect on the COD removal, followed by the initial pH of the solution. The current density has comparatively less significant effect on the response in individual operating parameters. The ANOVA indicated that the equation adequately represented the relationship between the responses and significant variables. As can be seen from the ANOVA results given in Table 6, all the quadratic coefficients and the interaction between pH and the current density have significant effects on the COD removal. The interaction effects between the current density and the electrolysis time and between pH and electrolysis time are insignificant on the COD removal. This confirmed high probability ((Prob > *F*) > 0.1) through the ANOVA [39–42]. Therefore, the interaction effect between these parameters will be removed from the RSM model for the COD removal. As can be seen from Table 5, the ANOVA of the color removal showed *F*-value of 29.42 implying that the model is significant. The ANOVA table obtained from the response surface quadratic model shows that the pH and current density have significant effects on the color removal whereas, X_1^2, X_3^2, and X_2X_3 are also significant terms (Table 7). For the orthophosphate removal, the model *F*-value and the corresponding *p*-value are determined to be 18.26 and 0.000044, respectively (Table 5). These values imply that the model is significant and can explain the relationship between the response and independent variables for the orthophosphate removal. As can be seen from the ANOVA results given in Table 8, the quadratic and interactive coefficients were found to be more significant than the linear coefficients. The ANOVA of the TSS and turbidity removal showed *F*-values of 6.92 and 14.99, respectively. Corresponding p values were determined to be 0.0028 and 0.00011, respectively, implying that the model is significant. It can be seen from Table 9 that the current

Table 4
Comparison of the actual and the predicted values of the COD, color, orthophosphate, TSS, and turbidity removal by electrocoagulation using Fe electrodes

	COD (%)		Color (%)		Orthophosphate (%)		TSS (%)		Turbidity (%)	
Run	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
1	76.65	77.7736	96.33	94.5688	99.53	99.5101	79.0	81.7129	99.16	99.4347
2	82.0	78.7657	99.77	100.186	98.8	98.8479	85.0	88.2573	98.0	97.88
3	83.0	79.2734	88.0	88.5843	99.6	99.6361	91.0	93.1353	98.5	98.5914
4	66.24	67.7555	92.0	91.0028	99.4	99.3665	83.0	83.1483	98.34	98.77
5	72.0	70.8562	88.0	89.8047	99.5	99.6325	78.0	81.4378	99.07	98.8656
6	67.13	70.7587	95.0	95.0013	99.42	99.4653	94.0	95.214	99.2	99.388
7	69.0	72.5959	92.66	93.1451	99.0	99.0485	95.0	94.9601	97.0	97.3823
8	61.2	59.9885	92.89	95.1434	99.17	99.2739	91.2	92.205	99.67	99.638
9	80.33	80.4847	80.0	79.8468	99.4	99.3536	84.0	81.8846	97.5	97.3742
10	69.16	68.8694	88.0	87.4619	98.96	98.9168	87.0	85.6738	98.2	98.0752
11	78.3	78.1813	99.77	99.888	99.42	99.3622	89.36	85.7829	99.0	99.0571
12	70.18	70.1618	95.18	94.3655	99.29	99.2576	95.74	95.8495	98.6	98.2904
13	78.0	80.2293	92.43	93.6575	99.37	99.3998	89.0	86.607	99.28	99.0682
14	68.02	65.6538	95.0	93.076	99.5	99.38	95.74	94.6654	99.2	99.1593
15	70.3	68.017	99.0	98.883	99.6	99.5849	90.0	89.476	99.4	99.3976
16	67.89	68.017	99.0	98.883	99.6	99.5849	90.1	89.476	99.42	99.3976
17	67.7	68.017	99.0	98.883	99.6	99.5849	90.05	89.476	99.47	99.3976
18	67.5	68.017	99.0	98.883	99.6	99.5849	90.0	89.476	99.5	99.3976
19	67.75	68.017	99.0	98.883	99.6	99.5849	90.2	89.476	99.4	99.3976
20	67.1	68.017	99.0	98.883	99.6	99.5849	90.0	89.476	99.45	99.3976

Table 5
The ANOVA of regression parameters of the predicted response surface quadratic model

Model	R^2	Adjusted R^2	Sum of squares	Mean square	F-value	Prob > F
Fe electrodes						
COD	0.89	0.79	618.5	68.7	9.28	0.00086
Color	0.96	0.93	515.3613083	57.26236759	29.42364085	0.000005
Ortophosphate	0.94	0.89	1.034191886	0.11491021	18.26055185	0.000044
TSS	0.86	0.73	404.3928073	44.93253415	6.929339951	0.0028
Turbidity	0.93	0.97	9.49125712	1.054584124	14.99132582	0.00011
Al electrodes						
COD	0.95	0.91	176.8891307	19.65434785	22.02180328	0.0000189
Color	0.87	0.76	9.602940564	1.066993396	7.566071064	0.001985827
Ortophosphate	0.93	0.87	1.578378462	0.175375385	15.09299566	0.00010549
TSS	0.85	0.71	2374.55929	263.8399211	6.089475385	0.004631397
Turbidity	0.88	0.77	72.00285957	8.00031773	8.080785847	0.00152352

Table 6
ANOVA results for the response surface quadratic model for the COD removal

	Fe electrodes						Al electrodes					
Source	Sum of squares	df	Mean square	F-ratio	p-value	Remark	Sum of squares	df	Mean square	F-ratio	p-value	Remark
Model	618.5	9	68.7	9.289	0.00086	Significant	176.89	9	19.65434	22.02	0.000019	Significant
X_1	135.123	1	135.123	18.26	0.0016	Significant	0.429773	1	0.429773	0.48	0.5035	Not significant
X_2	85.5167	1	85.5167	11.56	0.0068	Significant	10.2451	1	10.2451	11.48	0.0069	Significant
X_3	214.566	1	214.566	29.00	0.0003	Significant	86.7834	1	86.7834	97.24	<0.0001	Highly significant
X_1X_1	75.691	1	75.691	10.23	0.0095	Significant	8.04355	1	8.04355	9.01	0.0133	Significant
X_1X_2	78.6407	1	78.6407	10.63	0.0086	Significant	14.7882	1	14.7882	16.57	0.0022	Significant
X_1X_3	0.59653	1	0.59653	0.08	0.7822	Not significant	1.85607	1	1.85607	2.08	0.1799	Not significant
X_2X_2	59.5014	1	59.5014	8.04	0.0177	Significant	11.2709	1	11.2709	12.63	0.0052	Significant
X_2X_3	0.0288	1	0.0288	0.00	0.9515	Not significant	24.2208	1	24.2208	27.14	0.0004	Significant
X_3X_3	38.0949	1	38.0949	5.15	0.0466	Significant	9.84629	1	9.84629	11.03	0.0077	Significant
Total error	73.9816	10	7.39816				8.92495	10	0.892495			
Total	(corr.)		692.484	19					185.814	19		
$R^2 = 89.31\%$							$R^2 = 95.2\%$					

density and electrolysis time have significant effects on the TSS removal whereas, X_1^2 and X_1X_2 are also significant terms. The ANOVA study showed that pH has the most significant effect on turbidity removal followed by the current density (Table 10). X_1^2 and X_2^2 have highly sgnificant effects whereas, the interaction effect on turbidity removal between the current density and electrolysis time and the quadratic effect of electrolysis time are insignificant.

It can be seen from Table 5 that the correlation coefficient of the model for COD removal was determined to be 0.89. The value of correlation coefficient indicates that only 10.69% of the total variation could not be explained by the empirical model and

Table 7
ANOVA results for the response surface quadratic model for the color removal

	Fe electrodes						Al electrodes					
Source	Sum of squares	df	Mean square	F-ratio	p-value	Remark	Sum of squares	df	Mean square	F-ratio	p-value	Remark
Model	515.36	9	57.26	29.42	0.0000049	Highly significant	9.6	9	1.066993	7.56607	0.00198	Significant
X_1	58.0798	1	58.0798	29.84	0.0003	Significant	0.365248	1	0.365248	2.59	0.1386	Not significant
X_2	33.9648	1	33.9648	17.45	0.0019	Significant	1.18362	1	1.18362	8.39	0.0159	Significant
X_3	0.386837	1	0.386837	0.20	0.6652	Not significant	0.557712	1	0.557712	3.95	0.0748	Not significant
X_1X_1	372.508	1	372.508	191.41	<0.0001	Highly significant	1.46076	1	1.46076	10.36	0.0092	Significant
X_1X_2	5.14	1	5.14	2.64	0.1352	Not significant	1.83881	1	1.83881	13.04	0.0048	Significant
X_1X_3	0.088704	1	0.088704	0.05	0.8352	Not significant	2.37306	1	2.37306	16.83	0.0021	Significant
X_2X_2	4.84539	1	4.84539	2.49	0.1457	Not significant	0.468902	1	0.468902	3.32	0.0982	Not significant
X_2X_3	43.4778	1	43.4778	22.34	0.0008	Significant	1.8432	1	1.8432	13.07	0.0047	Significant
X_3X_3	47.8003	1	47.8003	24.56	0.0006	Significant	0.00591302	1	0.00591302	0.04	0.8419	Not significant
Total error	19.4613	10	1.94613				1.41023	10	0.141023			
Total (corr.)	534.823	19					11.0132	19				
$R^2 = 96.36\%$							$R^2 = 87.2\%$					

Table 8
ANOVA results for the response surface quadratic model for the ortophosphate removal

	Fe electrodes						Al electrodes					
Source	Sum of squares	df	Mean square	*F*-ratio	*p*-value	Remark	Sum of squares	df	Mean square	*F*-ratio	*p*-value	Remark
Model	1.034	9	0.115	18.26	0.000044	Highly significant	1.58	9	0.1753753	15.093	0.000105	Significant
X_1	0.191074	1	0.191074	30.36	0.0003	Significant	0.459364	1	0.459364	39.53	0.0001	Significant
X_2	0.00425249	1	0.00425249	0.68	0.4302	Not significant	0.253913	1	0.253913	21.85	0.0009	Significant
X_3	0.000880755	1	0.000880755	0.14	0.7161	Not significant	0.0896287	1	0.0896287	7.71	0.0195	Significant
X_1X_1	0.301544	1	0.301544	47.92	0.0001	Highly significant	0.271442	1	0.271442	23.36	0.0007	Significant
X_1X_2	0.077428	1	0.077428	12.30	0.0057	Significant	0.0605107	1	0.0605107	5.21	0.0456	Significant
X_1X_3	0.123137	1	0.123137	19.57	0.0013	Significant	0.150634	1	0.150634	12.96	0.0048	Significant
X_2X_2	0.118758	1	0.118758	18.87	0.0015	Significant	0.0349015	1	0.0349015	3.00	0.1137	Not significant
X_2X_3	0.25205	1	0.25205	40.05	0.0001	Significant	0.143112	1	0.143112	12.32	0.0056	Significant
X_3X_3	0.0597051	1	0.0597051	9.49	0.0116	Significant	0.05143	1	0.05143	4.43	0.0617	Not significant
Total error	0.0629281	10	0.00629281				0.116197	10	0.0116197			
Total (corr.)	1.09712	19					1.69458	19				
$R^2 = 94.26\%$							$R^2 = 93.14\%$					

Table 9
ANOVA results for the response surface quadratic model for the TSS removal

Fe electrodes							Al electrodes					
Source	Sum of squares	df	Mean square	*F*-ratio	*p*-value	Remark	Sum of squares	df	Mean square	*F*-ratio	*p*-value	Remark
Model	404.39	9	44.93	6.929	0.00281276	Significant	Model	2374.6	9	263.83992	6.089475	0.0046313
X_1	14.3808	1	14.3808	2.22	0.1673	Not significant	X_1	630.186	1	630.186	14.54	0.0034
X_2	70.4354	1	70.4354	10.86	0.0081	Significant	X_2	168.227	1	168.227	3.88	0.0771
X_3	76.7346	1	76.7346	11.83	0.0063	Significant	X_3	0.000908961	1	0.000908961	0.00	0.9964
X_1X_1	52.5548	1	52.5548	8.10	0.0173	Significant	X_1X_1	117.078	1	117.078	2.70	0.1312
X_1X_2	137.326	1	137.326	21.18	0.0010	Significant	X_1X_2	261.203	1	261.203	6.03	0.0339
X_1X_3	26.2805	1	26.2805	4.05	0.0718	Not significant	X_1X_3	3.25604	1	3.25604	0.08	0.7896
X_2X_2	2.82115	1	2.82115	0.44	0.5244	Not significant	X_2X_2	136.515	1	136.515	3.15	0.1063
X_2X_3	2.205	1	2.205	0.34	0.5727	Not significant	X_2X_3	6.78961	1	6.78961	0.16	0.7005
X_3X_3	2.11419	1	2.11419	0.33	0.5806	Not significant	X_3X_3	920.51	1	920.51	21.25	0.0010
Total error	64.8439	10	6.48439				Total error	433.272	10	43.3272		
Total (corr.)	469.237	19					Total (corr.)	2807.83	19			
$R^2 = 86.18\%$								$R^2 = 84.57\%$				

Table 10
ANOVA results for the response surface quadratic model for the turbidity removal

	Fe electrodes						Al electrodes					
Source	Sum of squares	df	Mean square	F-ratio	p-value	Remark	Sum of squares	df	Mean square	F-ratio	p-value	Remark
Model	9.49	9	1.054	14.99	0.0001	Significant	72.002	9	8.000317	8.08078	0.00152	Significant
X_1	0.492178	1	0.492178	7.00	0.0245	Significant	26.3475	1	26.3475	26.61	0.0004	Significant
X_2	0.350302	1	0.350302	4.98	0.0497	Significant	9.96215	1	9.96215	10.06	0.0100	Significant
X_3	0.0888726	1	0.0888726	1.26	0.2873	Not significant	8.05607	1	8.05607	8.14	0.0172	Significant
X_1X_1	4.4773	1	4.4773	63.65	<0.0001	Highly significant	9.54608	1	9.54608	9.64	0.0112	Significant
X_1X_2	1.50973	1	1.50973	21.46	0.0009	Significant	4.77493	1	4.77493	4.82	0.0528	Not significant
X_1X_3	2.16799	1	2.16799	30.82	0.0002	Significant	8.07003	1	8.07003	8.15	0.0171	Significant
X_2X_2	0.823081	1	0.823081	11.70	0.0065	Significant	1.8672	1	1.8672	1.89	0.1997	Not significant
X_2X_3	0.2048	1	0.2048	2.91	0.1188	Not significant	4.59045	1	4.59045	4.64	0.0567	Significant
X_3X_3	0.126572	1	0.126572	1.80	0.2095	Not significant	0.00388754	1	0.00388754	0.00	0.9513	Not significant
Total error	0.703463	10	0.0703463				9.90042	10	0.990042			
Total (corr.)	10.1947	19					81.9033	19				
$R^2 = 93.09\%$							$R^2 = 87.91\%$					

expresses good enough quadratic fits to navigate the design space. To express good enough quadratic fits to navigate the design space, the R^2 values should be at least 0.80 [43]. The correlation coefficients of the model for color and orthophosphate removal were determined to be 0.96 and 0.94, respectively (Table 5). Since the R^2 value obtained for the response variables were higher than 0.80, the result obtained indicated that the regression model explains the reaction well. Therefore, it can be concluded that the response surface model, developed in this study for predicting color and orthophosphate removal efficiencies, were considered to be satisfactory. As can be seen from Table 5, the R^2 values of the model for TSS and turbidity removal were found to be 0.86 and 0.93, respectively. The values of these correlation coefficients indicated that only 13.82 and 6.91% of the total variation could not be explained by the empirical model.

The second-order regression model obtained for the operating variables of the COD, color, orthophosphate, TSS, and turbidity removals by electrocoagulation, using Fe electrodes, were found to be satisfying, as the predicted vs. the observed value plot approximated along a straight line. The agreement between the actual and the predicted values of the color, orthophosphate, and turbidity removal is satisfactory and in accordance with the statistical significance of the quadratic model. Fairly moderate values of the correlation coefficients were obtained between the experimental and predicted responses for the COD and TSS removals. Numerical optimization, based on response surface and desirability functions, was used to determine the optimum process parameters for the maximum pollutant removal by electrocoagulation using Fe and Al electrodes. The optimized conditions under specified constraints obtained for the highest desirability are given in Table 11. The obtained results revealed that the maximum removal efficiencies were achieved using the predicted optimum values of each factor in the experiments, which were in good conformity with the predicted values.

3.1.2. Electrocoagulation using Al electrodes

The second-order model obtained for the COD, color, orthophosphate, TSS, and turbidity removal electrocoagulation using Al electrodes are given in Eqs. ((15)–(19)). The results of the ANOVA tests showed that the models were highly significant with low p-values and high F-values. The F-values and corresponding p-values obtained from the model show that the quadratic model is significant for the COD, color, ortophosphate, TSS, and turbidity removal by electrocoagulation using Al electrodes.

$$\text{COD removal}(\%) = 171.41 - 15.418 * X_1 - 0.8618 * X_2 - 1.0398 * X_3 + 0.5678 * X_1^2 + 0.1356 * X_1X_2 + 0.04804 * X_1X_3 - 0.0067 * X_2^2 + 0.0174 * X_2X_3 - 0.0062 * X_3^2 \quad (15)$$

$$\text{Color removal}(\%) = 103.541 - 0.2733 * X_1 - 0.0645 * X_2 - 0.1379 * X_3 - 0.2419 * X_1^2 + 0.04782 * X_1X_2 + 0.0543284 * X_1X_3 - 0.00136588 * X_2^2 - 0.0048 * X_2X_3 - 0.000153383 * X_3^2 \quad (16)$$

$$\text{Orthophosphate removal}(\%) = 103.57 - 1.5815 * X_1 + 0.07325 * X_2 - 0.0205 * X_3 + 0.1043 * X_1^2 - 0.0086 * X_1X_2 + 0.0136 * X_1X_3 + 0.0004 * X_2^2 - 0.0013 * X_2X_3 - 0.0005 * X_3^2 \quad (17)$$

$$\text{TSS removal}(\%) = 241.06 + 0.0015 * X_1 - 5.5320 * X_2 - 2.1651 * X_3 - 2.1664 * X_1^2 + 0.5699 * X_1X_2 - 0.0636 * X_1X_3 + 0.0233 * X_2^2 - 0.0092 * X_2X_3 + 0.0605 * X_3^2 \quad (18)$$

$$\text{Turbidity removal}(\%) = 100.54 + 1.4059 * X_1 - 0.0256 * X_2 - 0.2955 * X_3 - 0.6186 * X_1^2 + 0.0770 * X_1X_2 + 0.1001 * X_1X_3 - 0.0027 * X_2^2 - 0.0075 * X_2X_3 + 0.0001 * X_3^2 \quad (19)$$

As can be seen from equations, the individual operating variables, such as the initial pH of the solution, the current density, and the electrolysis time have net negative effect on the COD and color removal, whereas the pH and the electrolysis time have net positive effect on the orthophosphate removal. the The initial pH of the solution has positive effect, whereas the current density and the electrolysis time have net negative effect on the TSS and turbidity removal. The removal efficiencies presented in Table 12 were predicted by Eqs. ((15)–(19)).

The quadratic model statistical results are summarized in Table 5. Larger the F-value, the more significant is the corresponding term and the p-value

Table 11
Optimum operating conditions of the process variables

	Fe electrodes					Al electrodes				
Factor	COD	Color	Fosfat	TSS	Turbidity	COD	Color	Fosfat	TSS	Turbidity
pH	5.0	7.4782	5.96789	5.72947	8.98713	5.0	9	5	5	5.8
Current density	65.0	25.0	63.8796	64.9999	55.8485	50.5	50.5	65	25	65
Time	5.21	7.32748	5.00002	45.0	45.0	5.06	45	5	44.76	5

lower than 0.05 indicated the rejection of null hypothesis and the variable was said to be significant. The model *F*-value was determined to be 22.02 with corresponding *p*-value of 0.0000189 and high TSS value. These results implied that the model is significant and can appropriately explain the relationship between the response and independent variables for the COD removal. Based on these models, the significant model terms for the COD removal were significant except for X_1 linear term and X_1X_3 interactive term (Table 6). The ANOVA results of the color and orthophosphate removal showed *F*-values of 7.56 and 15.09 with p values of 0.0019 and 0.0001, respectively, for the quadratic model implying that the model is significant. It can be seen from Table 7 and 8 that all of the interactive model terms and X_2 in linear terms and X_1^2 in quadratic terms were found to be significant for color removal whereas, all of the linear and interactive model terms were found to be significant with only X_1^2 in quadratic terms for the orthophosphate removal. It can be seen from Table 5 that the model *F*-values were found to be large enough with the values of 6.09 and 8.08, respectively, for the TSS and turbidity removal to be evaluated as significant. The ANOVA results showed that X_1, X_1X_2, and X_3^2 model terms were determined to be significant for the TSS removal and all of the linear, interactive, and quadratic model terms were found to be significant, except for X_1X_2, X_2^2, and X_3^2 for the turbidity removal (Tables 9 and 10).

The surface response and contour plots of the quadratic model is given in Figs. 1–5. As can be seen from the Figs. 1–5 that one variable was kept at central level and the other two variables varied within the experimental ranges. In Figs. 1–5, the response surface and the contour plot were developed as a function of two variables within the experimental ranges of pH and time, while one variable was kept constant.

High correlation coefficients also ensure satisfactory adjustment of the quadratic model to the experimental data (Table 5). The determination coefficients of the model for the COD and orthophosphate removal were determined to be 0.95 and 0.93, respectively. The value of correlation coefficient indicated that only 5 and 7% of the total variation could not be explained by the empirical model. It can be concluded that the response surface model developed in this study for predicting the COD and orthophosphate removal efficiencies were considered to be satisfactory. The determination coefficients of the model for the color, TSS, and turbidity removal were determined to be 0.87, 0.85, and 0.88, respectively.

High correlations of the models were also evident in the prediction of the responses, in which the experimental results and the model (predicted) results obtained for the COD, color, and orthophosphate removal were in good agreement. Fairly moderate values of the correlation coefficients were obtained between the experimental and predicted responses for the TSS and turbidity removals. The fair correlation coefficients might have resulted by the insignificant terms and most likely due to three different variables selected in wide ranges with a limited number of experiments [34,44]. The optimized conditions under the specified constraints obtained for the highest desirability are given in Table 11. The obtained results revealed that the maximum COD removal efficiencies (98.91% for EC-Al and 98.84% for EC-Fe) and the orthophosphate removal efficiencies (99.78% for EC-Al and 98.24% for EC-Fe) were achieved using the predicted optimum values of each factor in the experiments which was in good conformity with the predicted values.

3.2. Sludge characterization by FT-IR

The information obtained from the FT-IR scanning was limited as the concentration of the functional groups on the sample surface were, in fact, very low, but the absorption bands and peaks provided the evidence of the presence of some surface functional groups. The main absorption peaks and the attribution of sludge, generated in electrocoagulation of dairy wastewater, is given in Table 13. In the FT-IR spectrum of sludge, generated in electrocoagulation of

Table 12
Comparison of the actual and predicted values of the COD, color, orthophosphate, TSS, and turbidity removal by electrocoagulation using Al electrodes

	COD (%)		Color (%)		Orthophosphate (%)		TSS (%)		Turbidity (%)	
Run	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
1	84.26	85.9068	99.77	99.565	99.0	99.1522	87.23	88.281	99.75	99.2921
2	81.22	81.9059	96.6	97.2201	98.75	98.7133	68.0	65.6121	92.47	93.1826
3	78.0	78.11	99.77	100.114	99.77	99.8458	89.36	85.2251	99.41	100.848
4	78.56	79.5339	99.54	99.6819	99.0	99.0599	90.0	85.3554	98.63	97.8209
5	77.0	76.7964	99.8	99.8128	99.0	98.9959	95.74	91.4114	99.86	100.226
6	74.0	74.7174	99.77	99.641	99.11	99.1045	71.0	66.1969	99.81	98.124
7	76.0	75.9596	98.9	98.4417	99.06	99.1545	92.0	84.6705	99.87	98.7518
8	80.0	79.3054	99.77	100.183	99.0	98.9161	91.5	82.2553	99.56	99.7324
9	82.65	82.3561	98.8	99.0603	99.9	99.7773	76.6	78.7862	99.78	99.466
10	82.2	81.701	98.9	98.4564	99.04	99.1001	47.0	53.702	93.68	94.337
11	80.0	78.9762	98.8	98.7429	98.94	98.9185	78.72	79.4765	96.62	96.9798
12	75.0	75.2249	99.77	99.6423	99.5	99.4584	82.0	90.1991	99.85	99.8357
13	83.35	82.0411	99.77	99.412	99.13	99.0359	99.0	99.5804	98.94	98.3255
14	72.0	72.51	99.77	99.9433	98.65	98.681	91.49	99.8652	99.81	100.77
15	80.08	79.7792	99.77	99.739	99.0	99.0394	72.0	75.5155	99.38	99.498
16	80.0	79.7792	99.77	99.739	99.0	99.0394	74.47	75.5155	99.79	99.498
17	79.8	79.7792	99.77	99.739	99.1	99.0394	74.0	75.5155	99.27	99.498
18	80.2	79.7792	99.77	99.739	99.2	99.0394	74.2	75.5155	99.25	99.498
19	79.65	79.7792	99.77	99.739	99.0	99.0394	74.6	75.5155	99.35	99.498
20	79.75	79.7792	99.77	99.739	99.0	99.0394	74.8	75.5155	99.6	99.498

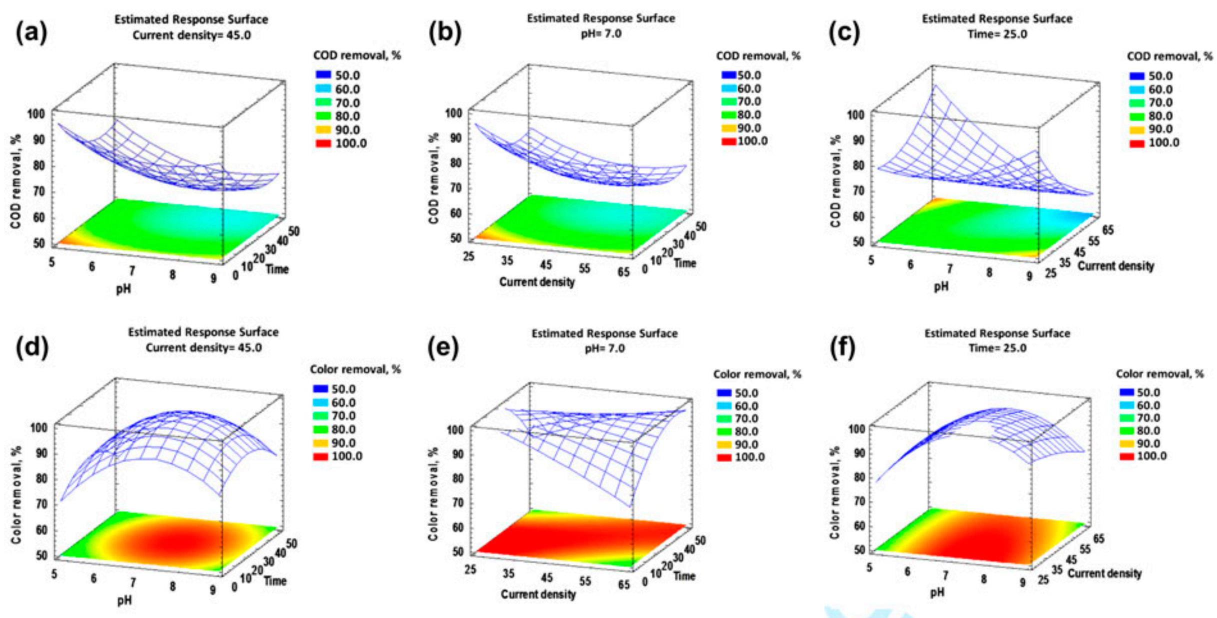

Fig. 1. Three-dimensional response surface graphs for the electrocoagulation treatment of dairy wastewater using Fe electrodes (a) COD removal vs. pH and contact time, (b) COD removal vs. current density and contact time, (c) COD removal vs. pH and current density, (d) Color removal vs. pH and contact time, (e) Color removal vs. current density and contact time, and (f) Color removal vs. pH and current density.

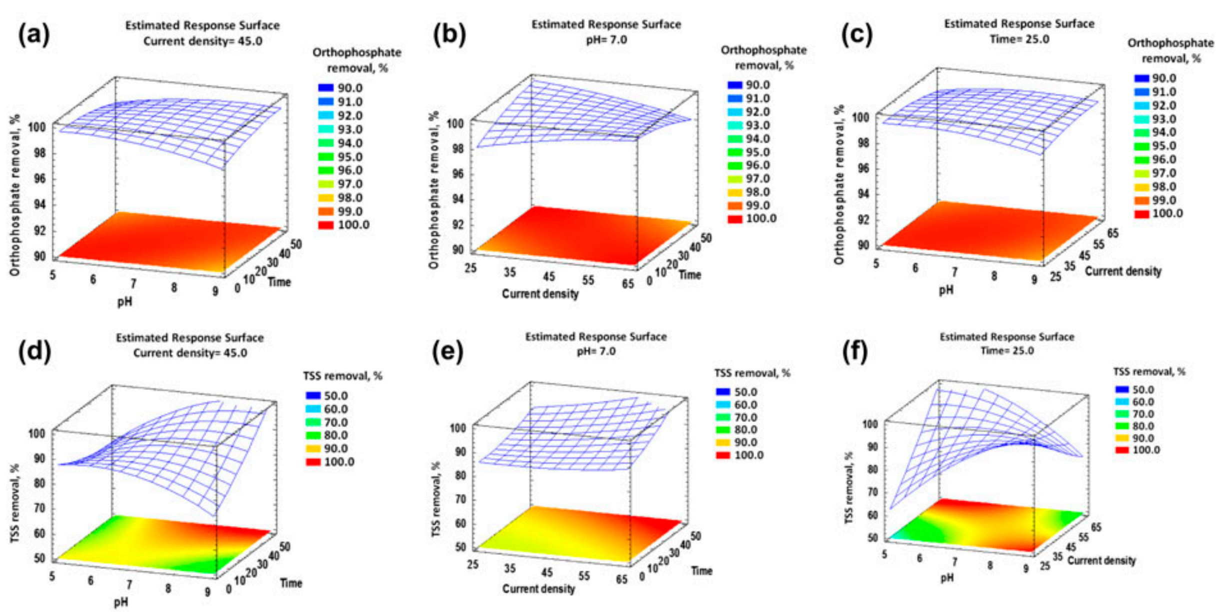

Fig. 2. Three-dimensional response surface graphs for the electrocoagulation treatment of dairy wastewater using Fe electrodes (a) Orthophosphate removal vs. pH and contact time, (b) Orthophosphate removal vs. current density and contact time, (c) Orthophosphate removal vs. pH and current density, (d) TSS removal vs. pH and contact time, (e) TSS removal vs. current density and contact time, and (f) TSS removal vs. pH and current density.

dairy wastewater, the peak at 3,271 cm^{-1} represented bonded and non-bonded hydroxyl groups which were attributed to adsorbed water. The peaks at 2,926 and 2,853 cm^{-1}, showing the presence of methylene group, can be attributed to the fat present in the wastewater, mainly. The peaks observed at 1,630 and 1,563 cm^{-1} can be assigned to protein amide I and amide II groups, respectively. The main absorbance in the

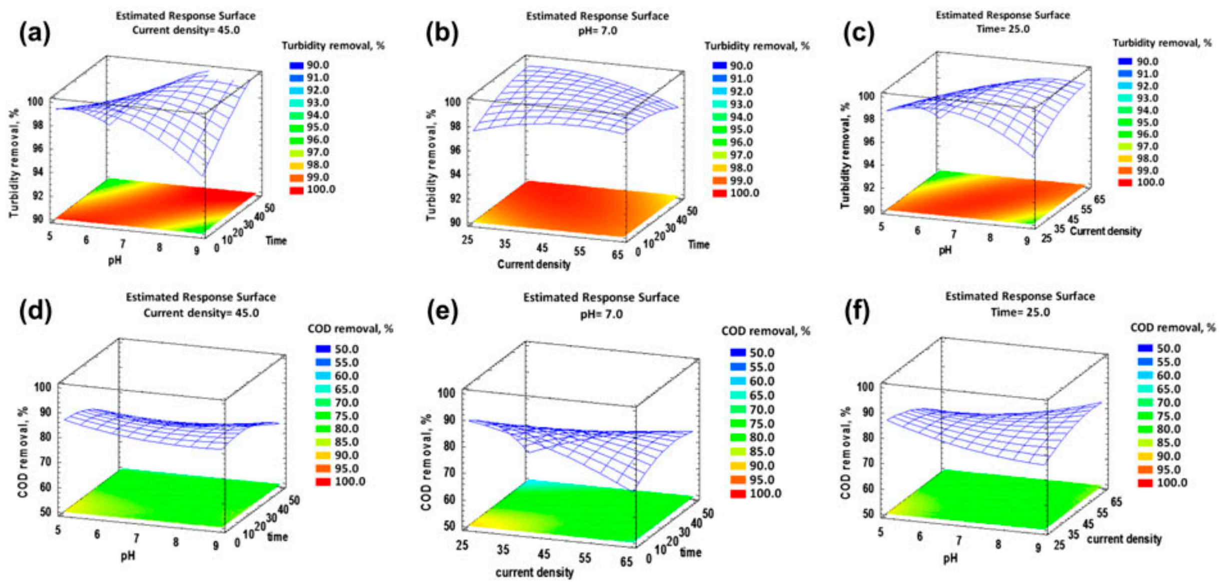

Fig. 3. Three-dimensional response surface graphs for the electrocoagulation treatment of dairy wastewater using Fe electrodes (a) Turbidity removal vs. pH and contact time, (b) Turbidity removal vs. current density and contact time, (c) Turbidity removal vs. pH and current density, (d) COD removal vs. pH and contact time, (e) COD removal vs. current density and contact time, and (f) COD removal vs. pH and current density.

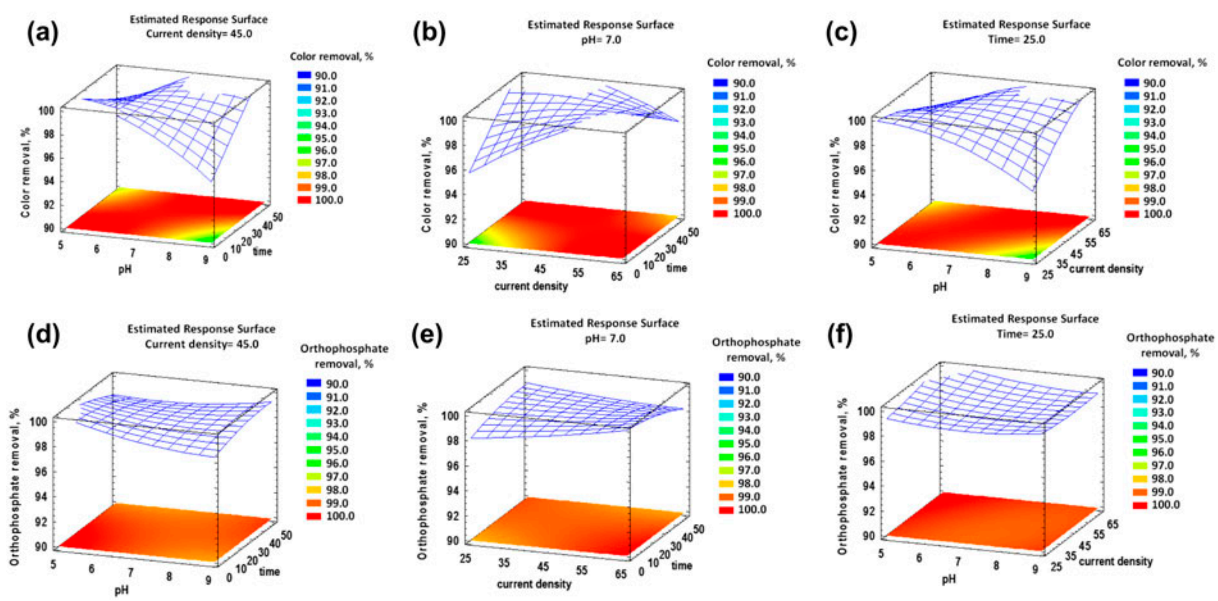

Fig. 4. Three-dimensional response surface graphs for the electrocoagulation treatment of dairy wastewater using Al electrodes (a) Color removal vs. pH and contact time, (b) Color removal vs. current density and contact time, (c) Color removal vs. pH and current density, (d) Orthophosphate removal vs. pH and contact time, (e) Orthophosphate removal vs. current density and contact time, and (f) Orthophosphate removal vs. pH and current density.

FT-IR spectra of sludge in the region of 1,150–1,030 cm^{-1} and centered on 1,115 cm^{-1} was associated with the pronounced concentration of carbohydrate in the sample. The band in the region 800–1,000 cm^{-1}, which was centered on 891 cm^{-1} and 980 cm^{-1}, was assigned as the carbohydrate ring. The peak observed at 704 cm^{-1}, representing amide group, can be attributed to protein. The peak which characterized Al–OH and Fe-OH bendings is represented by the bands at 1,100 cm^{-1} and 1,018 cm^{-1}, respectively. The obtained

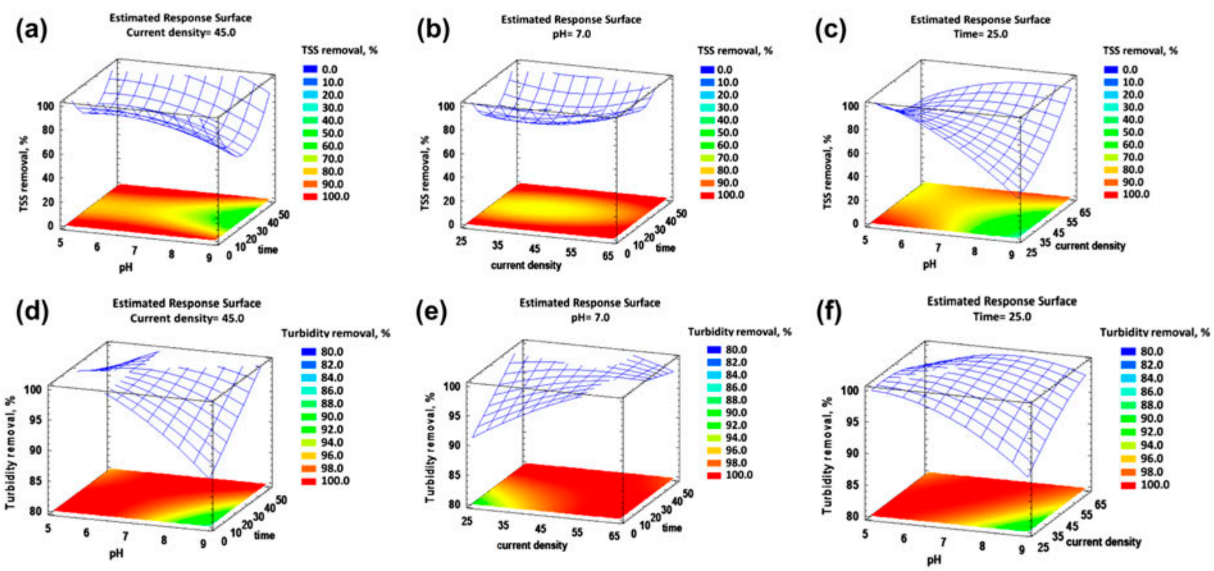

Fig. 5. Three-dimensional response surface graphs for the electrocoagulation treatment of dairy wastewater using Al electrodes (a) TSS removal vs. pH and contact time, (b) TSS removal vs. current density and contact time, (c) TSS removal vs. pH and current density, (d) Turbidity removal vs. pH and contact time, (e) Turbidity removal vs. current density and contact time, and (f) Turbidity removal vs. pH and current density.

FT-IR results highlighted that pollutants in dairy wastewater was linked with aluminum hydroxide and iron hydroxide complexes and additionally, generated sludge contained milk components. These results were consistent with the results concluded by Bensadok et al. [4].

3.3. Operational cost

Operational cost is one of the most important parameters that greatly determine the feasibility of any wastewater treatment process. The operating cost was calculated using the following equation [45,46].

Table 13
The main absorption peaks and the attribution of sludge generated in electrocoagulation of dairy wastewater

Wavelenght (cm^{-1})	Group	Attribution
3,271	O–H	Hydroxyl group
2,926	Methylene(–CH_2)	Fat mainly
2,853	Methylene(–CH_2)	Fat mainly
1,630	Carbonyl (C–O)	Protein (amide I)
1,563	N–H	Protein (amide II)
1,115	C–O C–C C–O–C	Carbohydrate
980	Carbohydrate ring	Carbohydrate
891	Carbohydrate ring	Carbohydrate
704	Amide (N–H)	Protein

$$\text{Operational cost} = aC_{\text{energy}} + bC_{\text{electrode}} + cC_{\text{chemicals}} \tag{20}$$

where C_{energy} is the energy consumption (kWh/m^3), $C_{\text{electrode}}$ is the electrode consumption (kg/m^3), and $C_{\text{chemicals}}$ is the chemical consumption (kg/m^3) of wastewater treated. The operational cost included labor, maintenance, and other fixed costs as well. The latter cost items were largely independent of the type of the electrode material [33,47]. In this study, energy and electrode material costs were taken into account as major cost items, in the calculation of the operating cost as €/m^3 wastewater treated at optimum conditions determined for the COD removal.

The electrical energy consumption was calculated using the following equation [33,48]:

$$C_{\text{energy}} = \frac{U \times i \times t_{\text{EC}}}{v} \tag{21}$$

where C_{energy} is the energy consumption (kWh/m^3), U is the applied voltage (V), I is the current intensity (A), t_{EC} is the electrocoagulation time (s), and V is the volume of the treated wastewater (m^3).

The amount of electrode dissolved was calculated theoretically using Faraday's law:

$$C_{\text{electrode}} = \frac{i \times t_{\text{EC}} \times M_w}{Z \times F \times V} \tag{22}$$

Table 14
Comparison of the results with similar works in literature

Research	Real Wastewater (R)/ Synthetic water (S)	Anode/ cathode material	Reactor type	Volume treated	Optimum conditions	Initial pollutant concentrations	Optimum removal efficiency	Optimum EEC	Optimum OC
Kushwaha et al. [1]	S	Fe	Batch	1,500 mL	270 A/m^2	COD: 3,900 mg/L	COD: 70%	~0.83 −30.0 kWh/m^3	0.051 −1.80 €/m^3
					50 min	Turbidity: 1,744 NTU	Turbidity: 100%		
					pH: 7	TS: 3,090 mg/L TN: 113 mg/L	TS: 48% TN: 93%		
Sengil and Ozacar [49]	R	Fe	Batch	650 mL	60 A/m^2	COD: 18,300 mg/L	COD: 98%	~0.055 kWh/m^3	–
					1 min	O & G: 4,570 mg/L	O & G: 99%		
					pH: 7	TSS: 10,200 mg/L			
Bazrafshan et al. [50]	R	Al	Batch	2000 mL	60 V	COD 7855.25 mg/L	COD: 98.8%	0.095 kwh/L	–
					60 min	BOD_5 mg/L 3486.3	BOD: 98%		
					pH: 7.24	TSS 1724.17 mg/L			
Bensadok et al. [4]	S	Al	Batch	250 mL	0.5 mA/cm^2	COD: 7,560 mg/L	COD: 80%	0.03 kWh/kg	
					2 min	Phosphate: 41 mg/L	Phosphate: 58%		
					pH: 6.6	Turbidity: 1,348 NTU	Turbidity: 96%.		
Tchamango et al. [6]	S	Al	Batch	2000 mL	50 A/m^2	Milk content: 1,000 mg/L	COD: 61%	–	–
					30 min pH: 7		Phosphorus: 89% Nitrogen: 81%		
This study	R	Al	Batch	600 mL	50.5 A/m^2 5.06 min pH: 5	COD: 788 mg/L TSS: 94 mg/L Orthophosphate: 6.91 mg/L Turbidity: 473 NTU Color: 436 Pt/Co	COD: 98.9% TSS: 92% Orthophosphate: 99.6% Turbidity: 98.6% Color: 98.9%	–	0.42 €/m^3

where $C_{electrode}$ (kg/m^3) is the iron or aluminum electrode consumption in the electrolytic cell, I is the current intensity (A), t_{EC} is the electrocoagulation time (s), M_w is the molecular mass of the electrode (g/mol), Z is the number of electron transferred ($Z_{Al} = 3$, $Z_{Fe} = 3$), F is the Faraday constant (96,487 C/mol), and V is the volume of the treated wastewater (m^3).

The reaction time and the current density exhibited similar effects on the process performance and the operating cost. The operational cost was calculated to be 0.54 and 0.42 € per m^3 dairy wastewater treated for iron and aluminum electrodes, respectively. The energy consumption and the electrode consumption were found to be higher in electrocoagulation process using iron electrodes than that of in the process using aluminum electrodes.

3.4. Evolution of art state with the application of electrocoagulation to dairy wastewater

The results of this study are summarized in Table 14 and also compared with the similar works concluded by the researchers [1,4,6,49–51]. Sengil and Ozacar [49] studied the effects of variables on the removal of COD and oil–grease from dairy wastewater in electrocoagulation of dairy wastewaters using mild steel electrodes and concluded that the overall COD and oil–grease removal efficiencies reached 98 and 99%, respectively. The mean energy consumption under the optimum conditions was found to be 0.003 kWh/kg COD. Tchamango et al. [6] compared electrocoagulation and chemical coagulation processes in dairy wastewater treatment and concluded that electrocoagulation process with aluminum electrodes was a convenient route for dairy wastewater treatment. The COD, phosphorus, nitrogen contents, and turbidity removal yields were found to be 61, 89, 81 and 100%, respectively. Bensadok et al. [4] investigated the electrochemical technique for the treatment of milk liquid fractions. The COD, phosphate, and turbidity removal was studied by varying the operating conditions. Under optimum conditions, the greatest removal efficiency (the removal yield of COD, phosphates and turbidity were respectively 80, 58 and 96%) was obtained by using Al electrodes. The energy consumption at optimum conditions was found to be 0.03 kWh/kg of COD removal. Kushwaha et al. [1] investigated the application of RSM to electrocoagulation of sythetic dairy wastewater using iron electrodes and concluded that the RSM was successfully employed for electrocoagulation treatment. At optimum conditions, the COD, TS, TN, and turbidity removal efficiencies were found to be 70, 48.2, 92.75 and 99.8%, respectively. The operational cost including both electricity and the electrode consumption were determined to be in the range of 0.051–1.80 €/m^3. Bazrafshan et al. [50] studied the effects of the operating parameters on a real dairy wastewater in the electrocoagulation process, using Al electrodes and obtained 98.84% COD removal, 97.95% BOD_5 removal, and 97.75% TSS removal efficiencies at optimum conditions. The energy consumption was found to be in the range of 0.012–0.095 kWh/L.

In conclusion, the results of this study were found to be consistent with the afore-mentioned studies from the point of pollutant removal efficiencies and operational cost analysis. The study differs from other studies from the points of incorporating the application of RSM with the comparison of Al and Fe electrodes utilization, sludge characterization, and optimal cost analysis in the electrocoagulation process of real dairy wastewater.

4. Conclusion

The present study attempted to investigate the applicability of electrocoagulation process using Fe electrodes in dairy wastewater treatment. The results of the study showed that electrocoagulation process could be an appropriate treatment alternative for dairy wastewater, providing high pollutant removal efficiency with low energy consumption. The treatment efficiency was found to be a function of the initial pH, current density, and electrolysis time. RSM has been successfully employed for electrocoagulation process of dairy wastewater. The influence of variables; initial pH, current density, and electrolysis time on the COD, color, orthophosphate, TSS, and turbidity removal was investigated. Three operational parameters were taken as input parameters in the range of pH: 5–9; J: 25–65 A/m^2, and t_{EC}: 5–45 min, whereas the COD, color, orthophosphate, TSS, and turbidity removal rates were taken as responses of the system. The quadratic model developed in this study showed the presence of a high correlation between the experimental and predicted values. ANOVA showed high determination of the coefficient values ($R^2 > 0.80$), thus, ensuring a satisfactory adjustment of the second-order regression model with the experimental data. Under the optimum values of process parameters, 98.91% COD and 99.78% orthophosphate removal efficiencies with Al electrodes, 98.84% COD and 98.24% orthophosphate removal efficiencies with Fe electrodes were obtained. The operational cost, including both the electricity and the electrode consumption at optimum conditions, were determined to be higher for Fe electrodes.

Consequently, the models could be used to navigate the design space. These plots indicated adequate agreement between the real data and the data obtained from the models. The low-error values in the experimental and predicted values indicated good agreement between the results achieved from the models and experiments. These results confirmed that the RSM was a powerful tool for optimizing the operational conditions of electrocoagulation for the COD, color, orthophosphate, TSS, and turbidity removals from dairy wastewater. Beside the advantages of application of electrocoagulation process to dairy industry, pH increase in electrocoagulation runs could be considered as a disadvantage of electrocoagulation process. The final pH inclined to increase toward basic values. Furthermore, the lower the initial pH, the higher the pH increase in electrocoagulation runs. To resolve this problem, neutralization was suggested after the application of electrocoagulation process to dairy industry. According to the optimum conditions determined by the application of RSM to obtain the maximum removal efficiencies, the pH of the dairy wastewater should be 5. To provide the optimum conditions, the pH of the emulsion to be treated should be adjusted to the desired level by neutralization process before treatment. The final pH of the wastewater, treated by electrocoagulation process at optimum conditions, was determined to be 7.23.

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